

## Surface Chemistry of Liquid Metals

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### Abstract

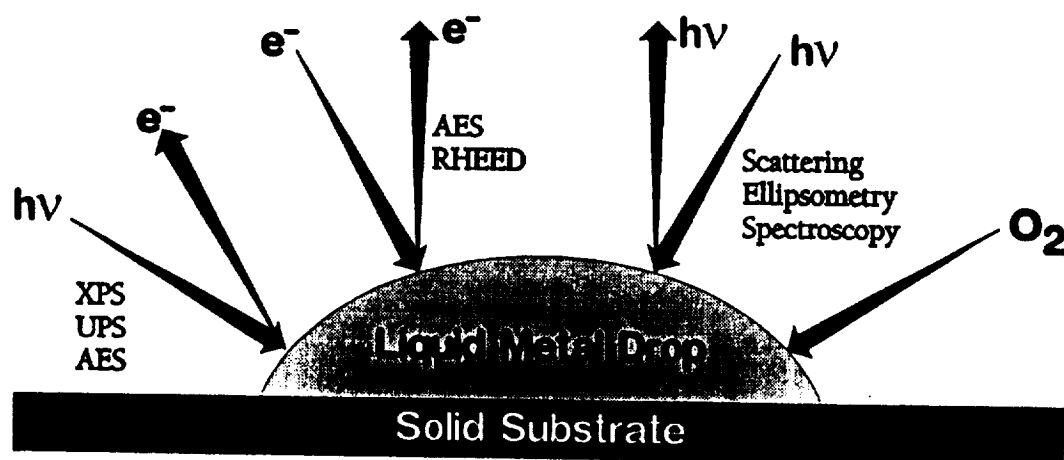
The fundamental surface chemistry of the behavior of liquid metals spreading on a solid substrate is not at all well understood. Figure 1 is a cartoon of a few of the questions that need to be studied.

Each of these questions involves knowing the details of the structure of interfaces and their dynamics. For example the structure of a monolayer of tin oxide on pure liquid tin is unknown. This is in contrast to the relatively large amount of data available on the structure of copper oxide monolayers on solid, pure copper. However, since liquid tin has a vapor pressure below  $10^{-10}$  torr for a reasonable temperature range above its melting point (Fig. 3), it is possible to use the techniques of surface science to study the geometric, electronic and vibrational structures of these monolayers.

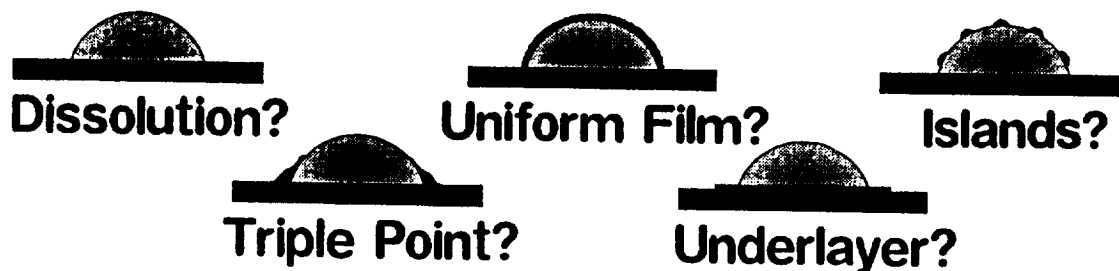
In addition, certain techniques developed by surface chemists for the study of liquid systems can be applied to the ultra-high vacuum environment. In particular we have shown that light scattering spectroscopy can be used to study the surface tension tensor of these interfaces. The tin oxide layer in particular is very interesting in that the monolayer is rigid but admits of bending. Ellipsometric microscopy allows the visualization of monolayer thick films and show whether island formation occurs at various levels of dosing.

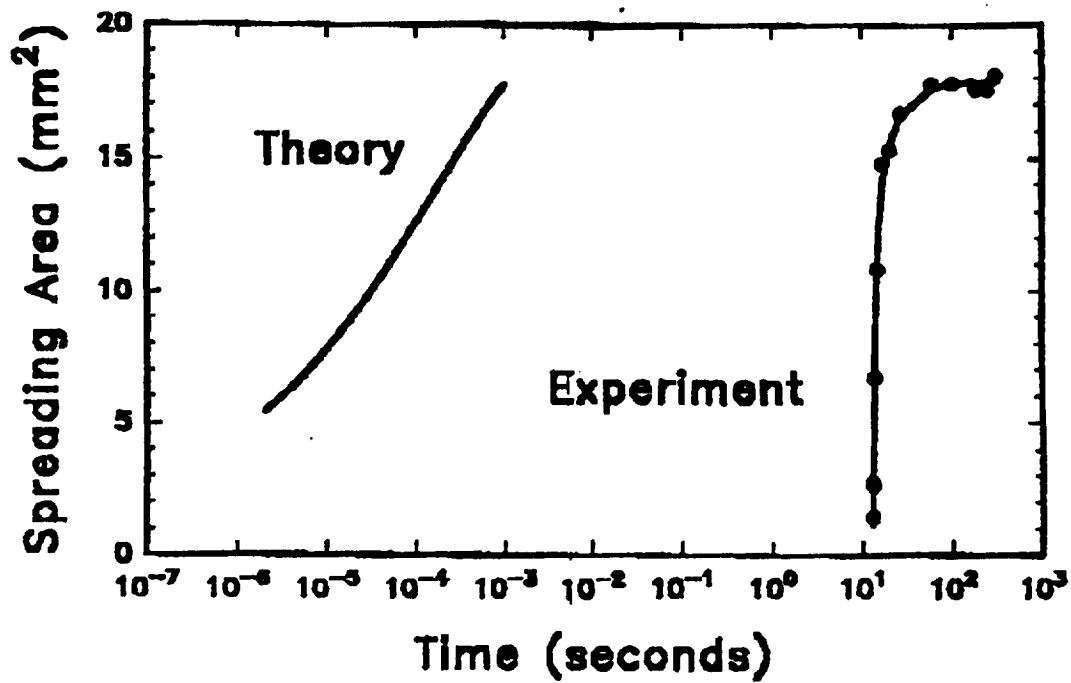
Figure 2 demonstrates how poorly the theory for simple liquids spreading on isotropic substrates works for the spreading of liquid tin on solid copper. We believe that the missing function in the theory is the reaction mechanism as copper-tin intermetallic compounds are formed at the tin-copper three phase contact line. It will require a considerable effort to develop the experimental data necessary for testing a better theory of spreading; the mathematical techniques are known and there are experimental techniques that can be tried. However, much needs to be done to improve accuracy and precision. Indeed, Figure 5 shows how poorly the surface tension of liquid tin is known. The use of ultra-high vacuum techniques are required; the components must start with very high purity. Only a few percent of impurities will lower the surface tension by 20 mN/m!

Figure 6 shows some literature data replotted. The message here is that the isotherm of oxygen chemisorbed on liquid tin develops a rigid monolayer; the two-dimensional compressibility for the tin oxide monolayer is smaller than the comparable organic monolayer. Reproducing and extending these results is a major task but will result in a much deeper understanding of both the structure and dynamics of these oxide systems. Figure 8 shows a schematic of a Brewster angle microscope from the work of J. Meunier's group at ENS in Paris. The optics is modified for liquid metal measurements to that of an ellipsometer since the tin surface is a conductor and so Brewster's angle is undefined. Preliminary work we have done suggests that the tin oxide monolayer is structured and not uniform.

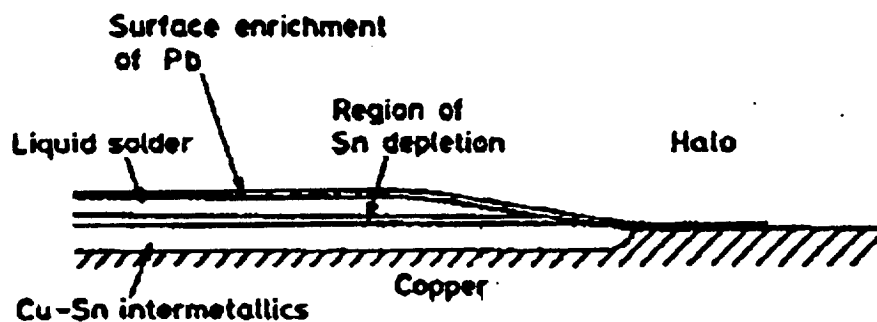


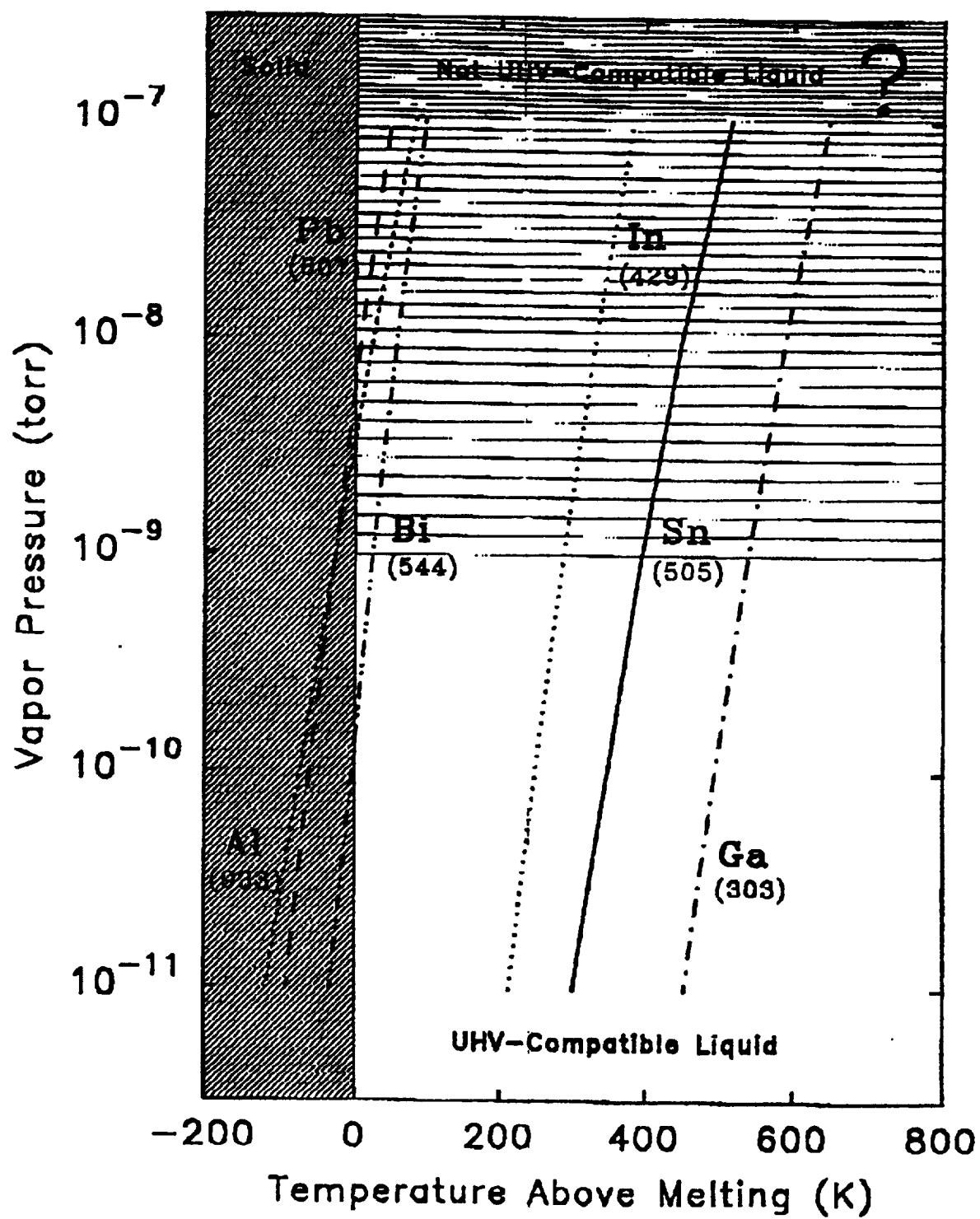
## How does the oxide form?





What is missing from the theory?





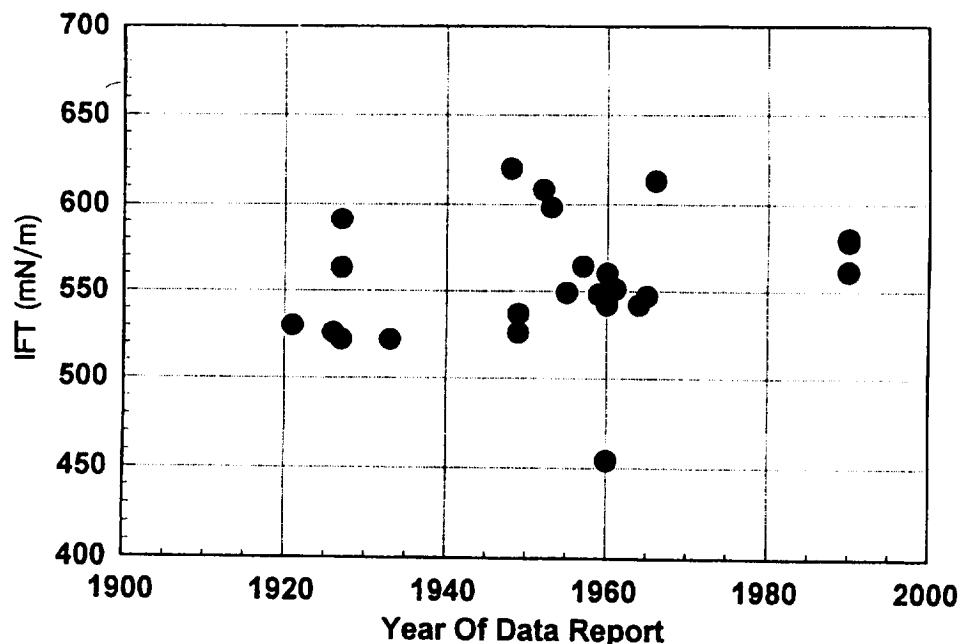
The literature concerning the surface tension liquid metals is of very poor quality.

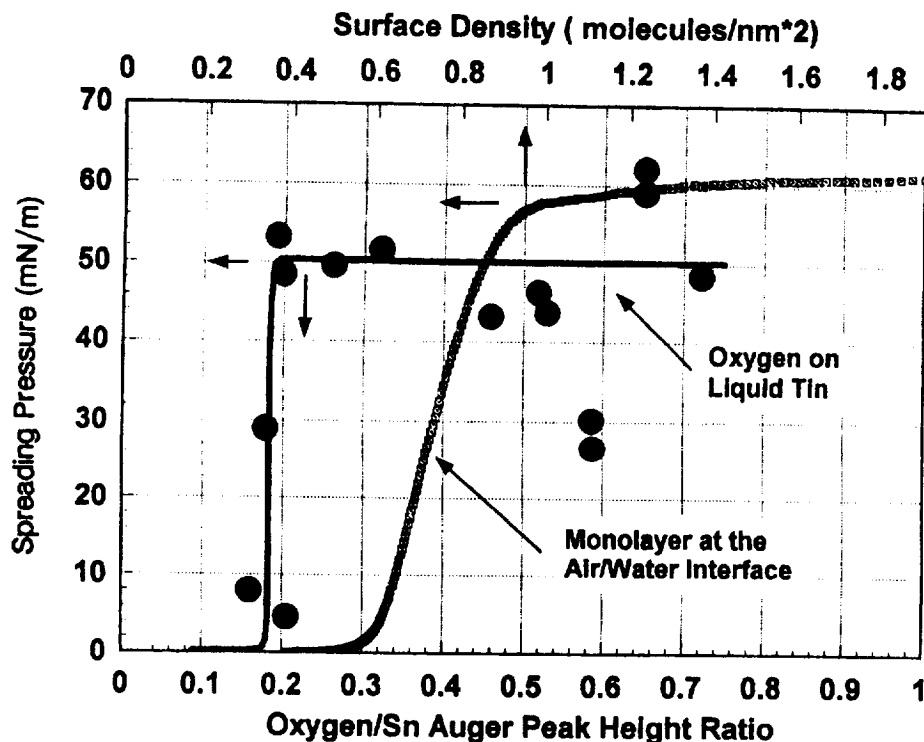
Only about ten papers meet the quality standards of surface science and surface chemistry.

The problem is that of surface contamination. For example oxide formation.

This can be overcome for certain metals: TIN is an example.

### The History of IFT Measurement For Liquid Tin at 250 deg C

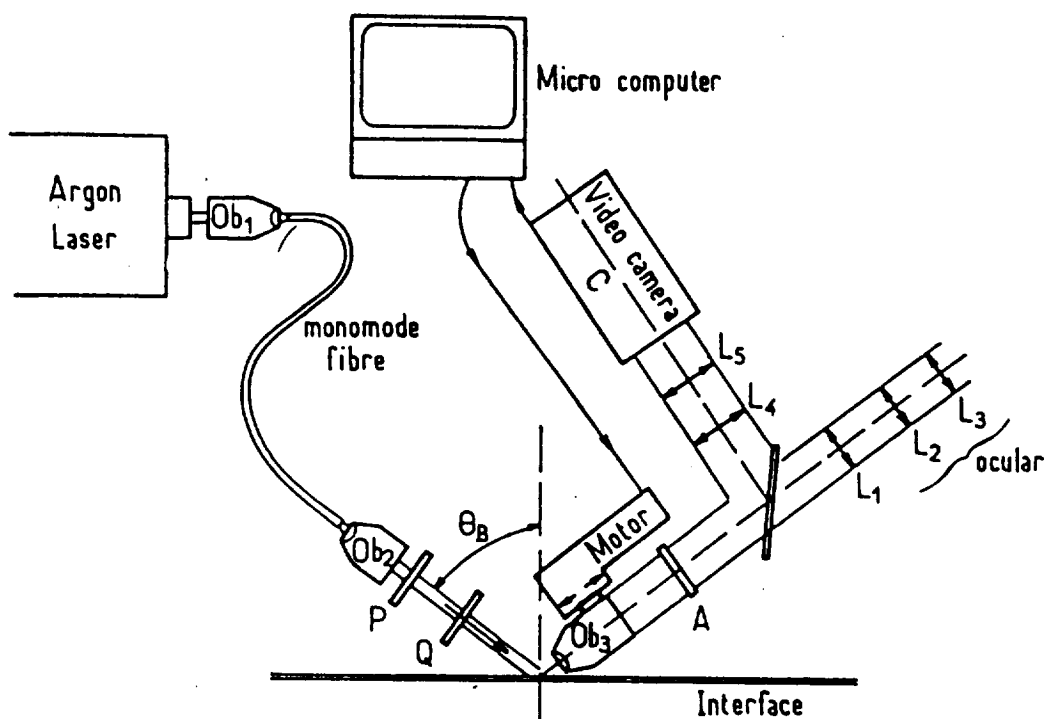




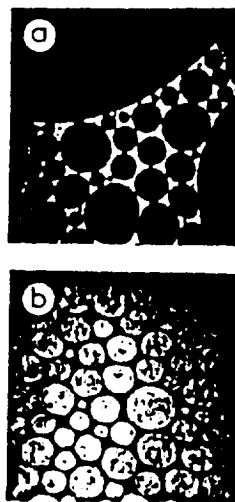
A classical monolayer spread at the air/water interface compared to an oxygen monolayer dosed onto liquid tin in UHV. Note the high precision of the data for the classical isotherm compared to the scatter of points for the liquid tin isotherm. The precision and accuracy of the liquid tin data can be improved greatly.

## EXPERIMENTAL TECHNIQUES

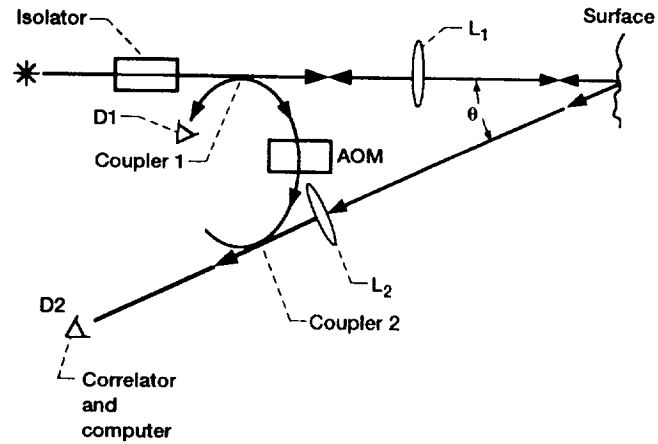
1. Auger, Photoelectron Spectroscopy. Surface Science
2. Light Scattering Spectroscopy
3. Ellipsometric Microscopy



Schematic diagram of the microscope at the Brewster angle. Ob<sub>1</sub>, Ob<sub>2</sub>, Ob<sub>3</sub>: microscope objectives; L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub>, L<sub>5</sub>: lens; P: polarizer (glan); A: (dichroic sheet); Q: quarter wave plate.

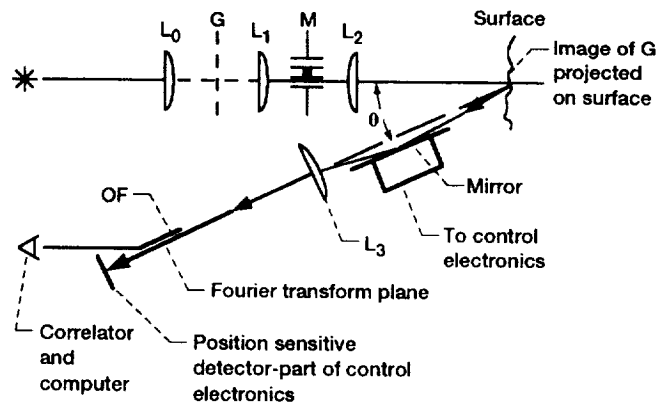


Images of a monolayer of myristic acid spread on water at pH = 2 and room temperature. (a) In the liquid-gas coexistence region; the area per molecule is about  $400 \text{ \AA}^2$ ; (b) in the liquid expanded-liquid condensed coexistence region; the area per molecule is about  $25 \text{ \AA}^2$ . The size of the pictures is  $200 \times 200 \text{ }\mu\text{m}$ .

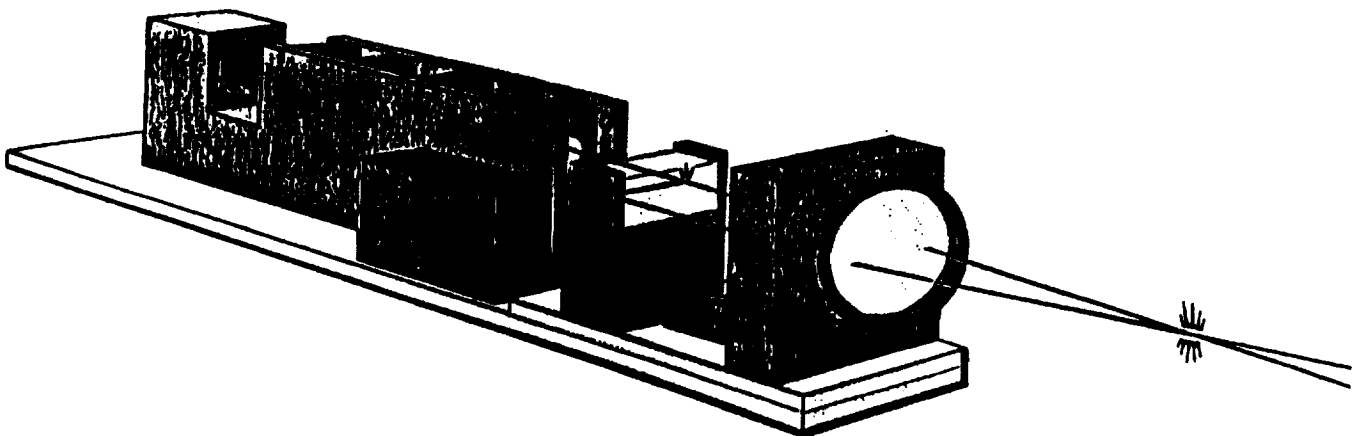


AOM - Acousto-Optic Modulator

Note: a delay line may be necessary in the reference fiber for exact phase matching at D2.



Optical fiber is placed so as to receive the grating order selected.





## **Results To Date**

- 1. A UHV system was modified to do the initial study of the oxide film.**
- 2. Structure changes were seen on liquid tin as oxygen was dosed**
- 3. The capillary ripple spectrum changed a great deal between half and full coverage.**
- 4. The microscopy system worked.**

